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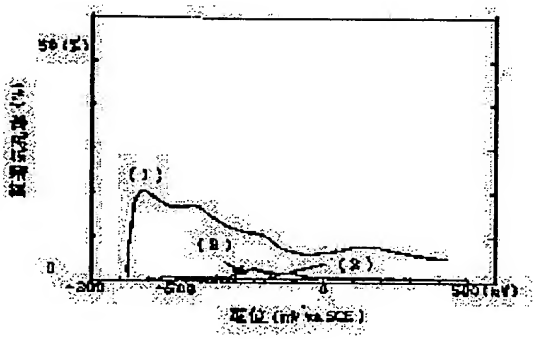
(54) PORE SEALING TREATMENT OF LAMINATED MATERIAL WITH INORGANIC COMPOUND

(57)Abstract:
PURPOSE: To reduce through pores in a coating film formed on the surface of a base material so as to obtain a laminated material by forming an inorg. compd. at the interface between the base material and the coating film.

CONSTITUTION: A laminated material obtd. by forming a coating film on the surface of a base material is subjected to ultrasonic treatment or vacuum treatment at the time of immersion in a sol in a sol-gel process. It is then dried and held at 150-1,500°C for a certain time. An inorg. compd. is formed at the interface between the base material and the coating film and through pores in the coating film are reduced.



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CLAIMS

[Claim(s)]
[Claim 1] The sealing method by the inorganic compound of the composite characterized by making it dry and carrying out fixed time amount maintenance of the composite which made the coat film form in a base material front face by the surface treatment method, and which consists of a base material and coat film under the temperature of further 150-1500 degrees C after adding sonication using a sol-gel method while being immersed in a sol solution.
[Claim 2] The sealing method by the inorganic compound of the composite according to claim 1 whose sonication is reduced pressure processing.
[Claim 3] The sealing method by the inorganic compound of the composite according to claim 1 whose sonication is sonication and reduced pressure processing.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] About the surface treatment method of the member used for an industrial machinery, this invention is making the interface of a base material and the coat film generate an inorganic compound in the composite which made the coat film form in a base material front face and which consists of a base material and coat film, and relates to the sealing method for decreasing the penetration pore of the coat film.
[0002]
[Description of the Prior Art] After what used organic compounds, such as resin, applies the sealing method of the former and said composite to a member to seal the organic compound or infiltrates it in the pore which is most, is immersed into the solution of an organic compound in the member itself, and contains the penetration pore of the coat film, the method of making it dry, heating depending on the case, and solidifying an organic compound is learned.
[0003]
[Problem(s) to be Solved by the Invention] There was a fault in which most organic compounds solidify on the front face of the coat film, a problem is in abrasion resistance since it is difficult to make the pore inside the coat film fully permeate, it will moreover decompose into by the sealing method by the aforementioned organic compound if it is weak with heat since sealer is an organic compound, and it becomes an elevated temperature, and sealing breaks, and the problem was in weatherability and endurance, and prolonged sealing maintenance was impossible.
[0004]
[Means for Solving the Problem] Made the coat film form in a base material front face by the surface treatment method that this invention should improve the above-mentioned fault. After adding sonication for the composite which consists of a base material and coat film using a sol-gel method while being immersed in a sol solution, It is made to dry, is characterized by carrying out fixed time amount maintenance under the temperature of further 150-1500 degrees C, and is characterized by replacing with the aforementioned sonication and performing reduced pressure processing, and sonication and reduced pressure processing.
[0005]
[Function] While composite is immersed in a sol solution, in order to add sonication or reduced pressure processing, it hydrolyzes, and the polymerization of the sol in a solution is carried out, and it is macromolecule-ized. And if this composite is dried, a sol will change to gel, organic [the amount of] will decompose by carrying out fixed time amount maintenance under the 150-1500-degree C further last temperature, and gel will become an inorganic compound. Moreover, in order that these reactions may add sonication or reduced pressure processing at the time of immersion, especially,

they are the interfaces of the coat film and a base material, will occur violently, and will carry out coat membrane formation of the base material preferentially. Consequently, the penetration pore between the coat film and a base material decreases substantially.

[0006]

[Example] As an example 1, the sealing method which used sonication together to the sol-gel method is explained. After carrying out blasting of the front face, thermal spraying of the alumina was carried out and the coat film was made to form using a rolled steel (SS400) as a base material. The thickness was about 250 micrometers. Next, sealing was performed to the composite which consists of this base material and coat film in the following procedures.

[0007] ** sol solution preparation-: -- stirring during about 30 minutes after adding the aluminum isopropoxide of a metal alkoxide at a rate of 10.22g and adding 0.5ml of HCl (1+1) solutions simultaneously to 90ml of water, and mixing -- carrying out -- further -- HCl(1+1)1.2ml -- in addition, do about 1-hour stirring and mixing of in a 75-degree C thermostat, and consider as a sol solution.

[0008] ** Immersion and sonication : while the composite degreased and washed in the acetone is immersed into the above-mentioned sol solution, adding sonication for about 10 minutes simultaneously and promoting the polymerization of a sol solution, combine alumina sol with a base material interface, especially a penetration pore side, and make membranes form.

[0009] ** Desiccation : make it dry for 30 minutes at the temperature of 105 degrees C in a dryer, and use as a gel object the sol made to form, after taking out composite out of a sol solution and making it season naturally.

[0010] ** Heat the composite heat-treated : dried at the temperature of 500 degrees C in an electric furnace for 1 hour.

[0011] Next, the sealing method which used reduced pressure processing together to the sol-gel method is explained as an example 2. Composite was the same as the example 1, and performed sealing in the following procedures.

[0012] ** sol solution preparation-: -- about 1-hour stirring after adding the aluminum isopropoxide of a metal alkoxide at a rate of 10.22g and adding 0.5ml of HCl (1+1) solutions simultaneously to 90ml of water, and mixing -- carrying out -- further -- HCl(1+1)10ml -- in addition, 40-degree C constant temperature -- ultrasonicate in the bottom for about 2 hours, do stirring and mixing of, and consider as a sol solution.

[0013] ** Immersion / reduced pressure processing : while the composite degreased and washed in ethanol is immersed into the above-mentioned sol solution, adding the reduced pressure processing by the aspirator for about 10 minutes simultaneously and promoting the polymerization of a sol solution, combine alumina sol with a base material interface, especially a penetration pore side, and make membranes form.

[0014] ** Desiccation : in a dryer, make it dry at the temperature of 90 degrees C for 1 hour, and use as a gel object the sol made to form, after picking out composite from a sol solution and making it season naturally.

[0015] ** Heat the composite heat-treated : dried at the temperature of 500 degrees C in an electric furnace for 1 hour.

[0016] Next, the sealing method which used together sonication and reduced pressure processing to the sol-gel method is explained as an example 3. After carrying out blasting of the front face, thermal spraying of the titania was carried out and the coat film was made to form using aluminum as a base material. The thickness was about 310 micrometers. And the following procedures performed sealing.

[0017] ** Preparation of a sol solution : add 56.5g of sodium silicate to 100ml of water, stir and mix for about 30 minutes, and consider as a sol solution.

[0018] ** Immersion and a supersonic wave, reduced pressure processing : while the composite degreased and washed in ethanol is immersed into the above-mentioned sol solution, adding sonication for about 5 minutes simultaneously and promoting the polymerization of about 2 hours, in addition a sol solution for the reduced pressure processing by the aspirator after that, combine a silica sol with a base material interface, especially a penetration pore side, and make membranes form.
** Desiccation and heat treatment : heat at the temperature of 150 degrees C in a dryer for 2 hours after picking out composite from a sol solution and making it season naturally.
[0019] Next, in order to check a result, the penetration porosity of the composite of the example 1 which performed sealing of this invention to the composite and this composite of non-sealing was measured with the electrochemical process (others [Moriaki / size]: an elevated-temperature institute magazine, 16 (1990) 332) which Assistant professor ©saka University welding operator study lab size Moriaki etc. developed. In drawing 1 , in order that the composite with which (1) has not carried out sealing, the composite with which (2) performed sealing of this invention, and (3) may look at that sealing by membrane formation is performed by the interface, after performing sealing by this invention, it grinds and about 200 micrometers is as a result of [of the composite except the alumina thermal-spraying film] measurement. From this result, it is observed that membranes are formed by the interface of a base material. Moreover, an example 2 and other examples are explained in drawing 2 . In drawing 2 , the composite of the example 2 which (1) has not sealed, the composite of an example 2 with which (2) performed sealing by reduced pressure of this invention, the composite with which (3) performed sealing by the supersonic wave of this invention using the sol solution of an example 2, and (4) are as a result of [of the penetration porosity by said electrochemical process of the composite which performed sealing by reduced pressure of the example 2 of this invention twice] measurement. Moreover, an example 3 is explained in drawing 3 and 4. After drawing 3 performs sealing of the example 3 of this invention, it is ground and is an electron microscope photograph on the front face of composite except the titania thermal-spraying film about 250 micrometers. Drawing 4 is the result of carrying out field analysis of the Si element by the X-ray microanalyser about the composite front face which performed the same processing as the above in order to look at that sealing is performed by the base material interface.
[0020] In addition, although said example is an example of the composite which made the coat film of the ceramics form in a metaled base material, it has the operation effectiveness that the composite which made a metal or the coat film of the ceramics form this in the base material of the ceramics is also equivalent. When a base material is the ceramics, it gets wet with an inorganic compound compared with a metal, ** is good, and in order to join together more firmly, it is because the result of better sealing is expectable compared with the composite whose base material is a metal. Moreover, it has the operation effectiveness that the composite which made the metaled coat film form in a metaled base material is also equivalent. Because, since the coat film is a metal from the ceramics, it is because coat membrane formation by the inorganic compound in the interface of the coat film and a base material is performed firmly.
[0021] Moreover, in said example, although the coat film is all a monolayer, the cascade screen which made membranes form by the wet galvanizing method and dry type vapor-plating method of the combination of a metal, the ceramics and a metal, a metal or the ceramics, and the ceramics also has the equivalent operation effectiveness. ** which stated this by the term of an operation -- like, since sealing is preferentially performed by the interface of a base material and the coat film, it is in

**.

[0022]

[Effect of the Invention] By performing sealing of this invention, manufacture of the composite which the penetration pore decreases substantially, consequently has corrosion resistance, thermal resistance, and weatherability can be attained, application to a wide range industrial machine member can be performed to the composite which has penetration pore, and big economic effects can be expected from it.

[Translation done.]

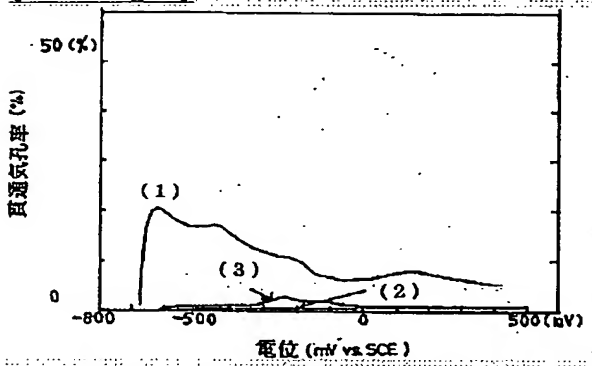
DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] It is the graph which shows the penetration porosity of the composite of non-sealing, and the composite of an example 1.
[Drawing 2] It is the graph which shows the penetration porosity of the composite of non-sealing, the composite of an example 2, and the composite of other examples.
[Drawing 3] After performing sealing of this invention, it is an electron microscope photograph on the front face of composite of the example 3 which carried out polish processing.
[Drawing 4] After performing sealing of this invention, it is as a result of [by the X-ray microanalyser on the front face of composite of the example 3 which carried out polish processing] field analysis.

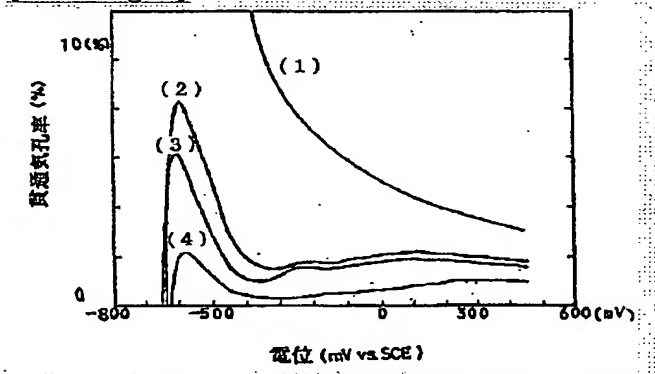
[Translation done.]

DRAWINGS

[Drawing 1]

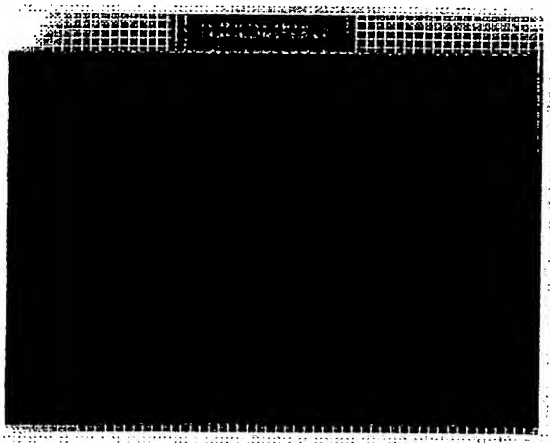


[Drawing 2]



[Drawing 3]

[Drawing 4]



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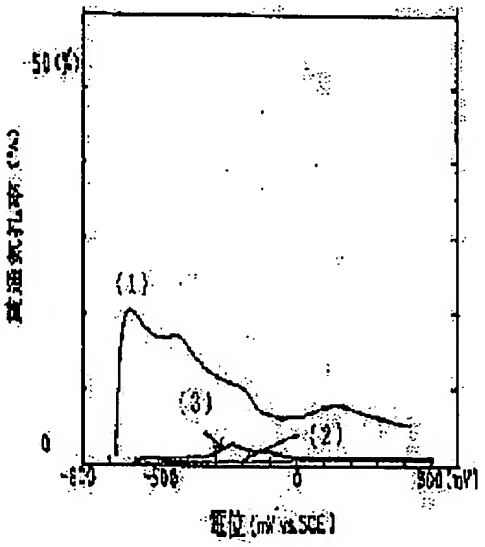
最終頁に続く

(54)【発明の名称】　複合材の無機化合物による封孔処理法

(57)【要約】
【目的】　基材と被覆膜からなる複合材において、無機化合物を、基材と被覆膜の界面に生成させて、被覆膜の貫通気孔を減少させようとするものである。
【構成】　基材表面に被覆膜を形成させた、基材と被覆膜からなる複合材に、ゾル・ゲル法を用い該ゾル・ゲル法の浸漬操作時に、超音波処理または減圧処理を加えた後、乾燥させ、さらに１５０～１５００℃の温度下で一定時間保持することで、基材と被覆膜の界面に無機化合物を生成させ、被覆膜の貫通気孔を減少させることを特徴とするものである。



【特許請求の範囲】
【請求項１】　表面処理法によって基材表面に被覆膜を形成させた、基材と被覆膜からなる複合材を、ゾル・ゲル法を用い、ゾル溶液に浸漬中に超音波処理を加えたのち、乾燥させ、さらに１５０～１５００℃の温度下で一定時間保持することを特徴とする複合材の無機化合物による封孔処理法。
【請求項２】　超音波処理が減圧処理である請求項１記載の複合材の無機化合物による封孔処理法。
【請求項３】　超音波処理が超音波処理及び減圧処理である請求項１記載の複合材の無機化合物による封孔処理法。
【発明の詳細な説明】
【０００１】
【産業上の利用分野】本発明は、産業用機械装置に用いられる部材の表面改質法に関するもので、基材表面に被覆膜を形成させた、基材と被覆膜からなる複合材において、基材と被覆膜の界面に無機化合物を生成させることで、被覆膜の貫通気孔を減少させる封孔処理法に係るものである。
【０００２】
【従来の技術】従来、前記複合材の封孔処理法は、樹脂などの有機化合物を用いたものがほとんどであり、その有機化合物を封孔したい部材に塗布したり、あるいは部材自身を有機化合物の溶液中に浸漬することで、被覆膜の貫通気孔を含む気孔内にしみ込ませたのち、乾燥させ、場合によっては、加熱して有機化合物を固化させる方法が知られている。
【０００３】
【発明が解決しようとする課題】前記の有機化合物による封孔処理法では、大部分の有機化合物が被覆膜の表面で固化し、被覆膜内部の気孔に十分に浸透させることが困難なため、耐摩耗性に問題があり、しかも、封孔剤が有機化合物であるため熱に弱く、高温になると分解して封孔が壊れる欠点があり、また耐候・耐久性に問題があって長期間の封孔維持は不可能であった。
【０００４】
【課題を解決するための手段】本発明は前述の欠点を改善すべく、表面処理法によって基材表面に被覆膜を形成させた、基材と被覆膜からなる複合材を、ゾル・ゲル法を用い、ゾル溶液に浸漬中に超音波処理を加えたのち、乾燥させ、さらに１５０～１５００℃の温度下で一定時間保持することを特徴とするものであり、また前記の超音波処理に代えて、減圧処理や、超音波処理及び減圧処理を行うことを特徴とするものである。
【０００５】
【作用】複合材をゾル溶液に浸漬するとともに、超音波処理あるいは減圧処理を加えるため、溶液中のゾルは加水分解され、重合し高分子化する。そして、該複合材を乾燥させると、ゾルはゲルに変化し、さらに、最終の１５０～１５００℃の温度下で一定時間保持することで有機分が分解して、ゲルは無機化合物になる。またこれらの反応は浸漬時に超音波処理あるいは減圧処理を加えるため、特に被覆膜と基材との界面で、激しく起こり、優先的に基材を被覆成膜することとなる。この結果、被覆膜と基材間の貫通気孔が大幅に減少する。
【０００６】
【実施例】実施例１として、超音波処理をゾル・ゲル法に併用した封孔処理法について説明する。基材として圧延鋼材（ＳＳ４００）を用い、その表面をブラストした後アルミナを溶射して被覆膜を形成させた。その膜厚は、約２５０μｍであった。つぎに、この基材と被覆膜からなる複合材に以下の手順で封孔処理を施した。
【０００７】ゾル溶液の調製：水９０ｍｌに対し、金属アルコキシドのアルミニウムイソプロポキシドを１０．２２ｇの割合で加え、同時にＨＣｌ（１＋１）溶液を０．５ｍｌ加えた後、約３０分間撹はん・混合し、さらにＨＣｌ（１＋１）１．２ｍｌを加えて、７５℃の恒温槽中で約１時間撹はん・混合して、ゾル溶液とする。
【０００８】浸漬・超音波処理：アセトン中で脱脂・洗浄した複合材を、上記ゾル溶液中に浸漬し、同時に超音波処理を約１０分間加え、ゾル溶液の重合を促進させると共に、基材界面、特に貫通気孔面にアルミナゾルを結合させ成膜させる。
【０００９】乾燥：複合材をゾル溶液中から取り出して、自然乾燥させた後、乾燥機中で１０５℃の温度で３０分間乾燥させ、成膜させたゾルをゲル体とする。
【００１０】熱処理：乾燥させた複合材を、電気炉中で５００℃の温度で、１時間加熱する。
【００１１】次に、実施例２として、減圧処理をゾル・ゲル法に併用した封孔処理法について説明する。複合材は実施例１と同じもので、以下の手順で封孔処理を施した。
【００１２】ゾル溶液の調製：水９０ｍｌに対し、金属アルコキシドのアルミニウムイソプロポキシドを１０．２２ｇの割合で加え、同時にＨＣｌ（１＋１）溶液を０．５ｍｌ加えた後、約１時間撹はん・混合し、さらに、ＨＣｌ（１＋１）１０ｍｌを加えて、４０℃の恒温下で超音波処理を約２時間行なって撹はん・混合し、ゾル溶液とする。
【００１３】浸漬・減圧処理：エタノール中で脱脂・洗浄した複合材を、上記ゾル溶液中に浸漬し、同時にアスピレータによる減圧処理を約１０分間加え、ゾル溶液の重合を促進させると共に、基材界面、特に貫通気孔面にアルミナゾルを結合させ成膜させる。
【００１４】乾燥：複合材をゾル溶液から取り出して、自然乾燥させた後、乾燥機中で、９０℃の温度で１時間乾燥させ、成膜させたゾルをゲル体とする。
【００１５】熱処理：乾燥させた複合材を、電気炉中で、５００℃の温度で１時間加熱する。

【００１６】次に、実施例３として超音波処理及び減圧処理を、ゾル・ゲル法に併用した封孔処理法について説明する。基材としてアルミニウムを用い、その表面をブラストした後チタニアを溶射して被覆膜を形成させた。その膜厚は、約３１０μｍであった。そして、以下の手順で封孔処理を行った。

【００１７】ゾル溶液の調製：水１００ｍｌに、ケイ酸ソーダ５６．５ｇを加え、約３０分間撹はん・混合しゾル溶液とする。

【００１８】浸漬・超音波，減圧処理：エタノール中で脱脂・洗浄した複合材を、上記ゾル溶液中に浸漬し、同時に超音波処理を約５分間加え、その後アスピレータによる減圧処理を約２時間加えて、ゾル溶液の重合を促進させると共に、基材界面、特に貫通気孔面にシリカゾルを結合させ成膜させる。

乾燥・熱処理：複合材をゾル溶液から取り出して、自然乾燥させた後、乾燥機中で、１５０℃の温度で２時間加熱する。

【００１９】次に成果を確認するため、未封孔の複合材及び該複合材に、本発明の封孔処理を施した実施例１の複合材の貫通気孔率を、大阪大学溶接工学研究所大森明助教授他が開発した電気化学的方法（大森明他：高温学会誌，１６（１９９０）３３２）で測定した。図１において、（１）は封孔をしていない複合材、（２）は本発明の封孔処理を施した複合材、（３）は界面で成膜による封孔が行われているのを見るため、本発明による封孔処理を施した後、研磨してアルミナ溶射膜を約２００μｍ除いた複合材の測定結果である。この結果から、基材の界面で成膜されているのが観測される。また、実施例２及びその他の実施例を図２において説明する。図２で、（１）は封孔していない実施例２の複合材、（２）は本発明の減圧による封孔処理を施した実施例２の複合材、（３）は実施例２のゾル溶液を用い、本発明の超音波による封孔処理を施した複合材、（４）は本発明の実施例２の減圧による封孔処理を２回施した複合材の、前記電気化学的方法による貫通気孔率の測定結果である。また、実施例３を図３，４において説明する。図３は本発明の実施例３の封孔処理を施した後、研磨してチタニア溶射膜を約２５０μｍ除いた複合材表面の電子顕微鏡写真である。図４は、封孔が基材界面で行われているのを見るため、前記と同じ処理を施した複合材表面について、Ｘ線マイクロアナライザーでＳｉ元素を面分析した結果である。

【００２０】なお、前記実施例は、金属の基材にセラミックスの被覆膜を形成させた複合材の例であるが、これをセラミックスの基材に金属又はセラミックスの被覆膜を形成させた複合材でも、同等の作用効果を有するものである。それは、基材がセラミックスの場合、金属に比べて無機化合物と濡れがよく、より強固に結合するため、基材が金属である複合材に比べて、よりよい封孔の結果が期待できるためである。また、金属の基材に金属の被覆膜を形成させた複合材でも、同等の作用効果を有する。なぜなら、被覆膜がセラミックスから金属になっているため、被覆膜と基材の界面での無機化合物による被覆成膜が強固に行われるためである。

【００２１】また、前記実施例では、いずれも被覆膜が単層であるが、金属とセラミックスや、金属と金属、またはセラミックスとセラミックスの組合せの、逐式めっき法や乾式気相めっき法で成膜させた積層膜でも、同等の作用効果を有するものである。これは、作用の項で述べたように、封孔が基材と被覆膜の界面で優先的に行われることから明かである。

【００２２】

【発明の効果】貫通気孔を有する複合材に、本発明の封孔処理を施すことで、その貫通気孔が大幅に減少し、その結果、耐食性，耐熱性及び耐候性を有する複合材の製造が可能となり、広範囲な産業用機械部材への適用が行え、大きな経済効果が期待できる。

【図面の簡単な説明】

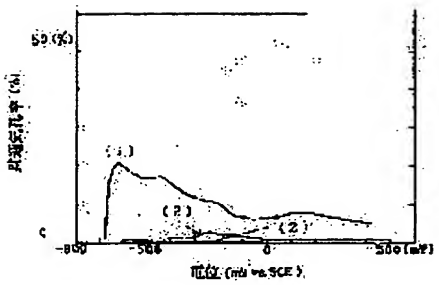
【図１】未封孔の複合材及び実施例１の複合材の貫通気孔率を示すグラフである。

【図２】未封孔の複合材，実施例２の複合材及び他の実施例の複合材の貫通気孔率を示すグラフである。

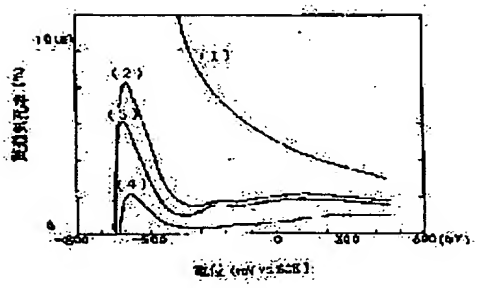
【図３】本発明の封孔処理を施した後，研磨処理した実施例３の複合材表面の電子顕微鏡写真である。

【図４】本発明の封孔処理を施した後，研磨処理した実施例３の複合材表面のＸ線マイクロアナライザーによる面分析結果である。

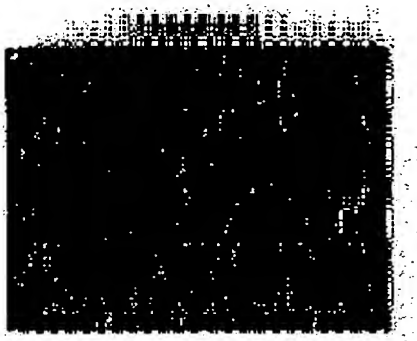
【図1】



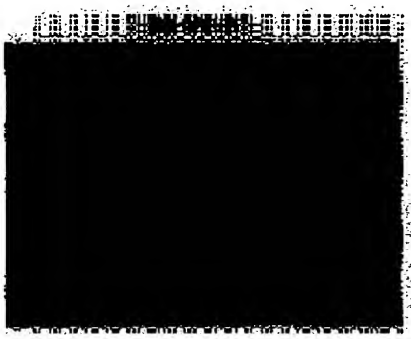
【図2】



【図3】



【図4】



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